Volume 18, No. 4 July/August 1996 Sandia National Laboratories

Probing flames with infrared cavity ringdown absorption spectroscopy

Jim Scherer, Dirk Voelkel from the University of Göttingen (Germany), and David Rakestraw have recently employed an innovative spectroscopy as a new diagnostic tool in the Diagnostics and Flame Chemistry Laboratory. Infrared cavity ringdown spectroscopy was developed at Sandia in collaboration with Dr. Anthony O'Keefe of Los Gatos Research and Professor Richard Saykally of U.C. Berkeley.

This research was motivated by the desire to exploit the information-rich mid-infrared spectral region, where many chemical species can be identified simultaneously by their unique spectral signatures. The cavity ringdown technique is an extremely sensitive absorption-based method capable of detecting trace species at sub-ppm levels in combustion environments. It is orders of magnitude more sensitive

than many other absorption-based methods, such as Fourier transform spectroscopy.

The cavity ringdown experiment is depicted in Figure 1. Pulsed infrared light is generated in a single mode optical parametric laser system and is injected into an optical cavity that comprises two highly reflective mirrors ($R \ge 99.98\%$). The rate of decay of light inside the cavity is monitored at the output mirror and is directly proportional to the net transmissivity of the cavity, including molecular absorption for species between the mirrors. Comparison of the cavity decay or "ringdown" time of an empty cavity to a cavity with a flame inside allows absolute absorption intensities to be obtained easily, from which molecular concentrations may be deduced.

Jim and David are utilizing this method to obtain (1-D) spatially resolved spectra of important combustion species in laminar flames. Typical data are presented in Figure 2, which shows the absorption spectrum obtained in a 35-Torr methane/air flat flame as a function of height above the burner surface. As combustion proceeds, methane features disappear while transitions due to intermediates (OH) and products (H_2O) arise. The absorption data can be deconvolved to yield concentration profiles to compare with flame kinetics models.

The high-sensitivity cavity ringdown technique complements other diagnostic techniques such as DFWM, LIF, and coherent anti-Stokes Raman scattering, and should enable the study of important combustion intermediates, such as CH₃, CH, and HO₂.

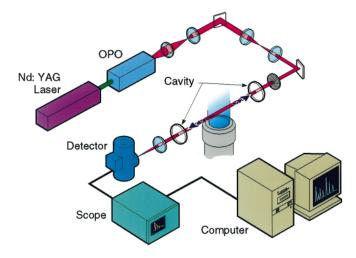


Figure 1. Schematic of the cavity ringdown apparatus employed to obtain high resolution infrared spectra in low pressure flames.

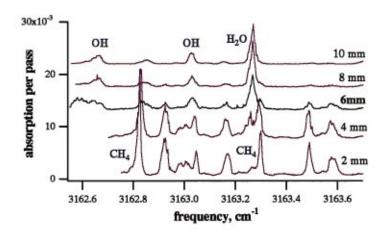


Figure 2. Cavity ringdown spectra as a function of height above the burner surface obtained in a low pressure methane/air flame. The visible flame front is located at 6 mm, consistent with the disappearance of methane features.

Technique developed for measuring ultraweak ultrashort laser pulses

All laser diagnostics involve the measurement of laser light, and sometimes very small amounts of it. When ultrashort (< 10⁻¹² sec) laser pulses are involved, the added difficulty of obtaining high time resolution makes the problem of measuring such weak pulses even harder. Recently, however, Sandia researchers solved this problem for even the weakest and fastest laser pulses. The team consisted of Rick Trebino, David Fittinghoff, graduate student Jason Bowie (University of California, Berkeley), Ken DeLong, and John Sweetser.

Previously, this team had solved the difficult problem of measuring highenergy ultrashort laser pulses with a technique they named Frequency-Resolved Optical Gating (FROG). FROG is rapidly becoming the standard technique for measuring highenergy ultrashort laser pulses. But FROG requires a nonlinear-optical medium and hence is limited to pulses of 10^7 photons or greater.

In collaboration with Ian Walmsley of the University of Rochester, these researchers realized that ultraweak ultrashort light pulses are almost always created from much stronger ultrashort pulses. As a result, the stronger pulse can be measured using FROG and then can be used as a reference pulse for measuring the ultraweak pulse, significantly simplifying the problem.

Indeed, simply measuring the spectrum of the sum of the known (strong) and unknown (ultraweak) pulses is sufficient to fully determine the unknown ultraweak pulse. Called Temporal Analysis by Dispersing a Pair Of Light E-fields (TADPOLE), this technique has allowed the measurement of a train of pulses with less than one photon per pulse.

Figure 1 shows the TADPOLE apparatus in a generic application, and Fig. 2 shows the measured TADPOLE spectrum of a pulse and also the retrieved pulse in conjunction with a corroborating measurement of the pulse using FROG.

TADPOLE is extremely sensitive because it involves no optical nonlinearities, takes advantage of CCDcamera technology, and is a type of heterodyne technique in which the weak pulse is effectively amplified by co-propagating with a stronger pulse.

Its simplicity and sensitivity make TADPOLE ideal for measuring signal pulses in a wide variety of diagnostics. It was developed for inverse-scattering problems for a Sandia Laboratory-Directed Research and Development project, but it will also be useful for ultrasensitive absorption-spectroscopy measurements in flames and other media.

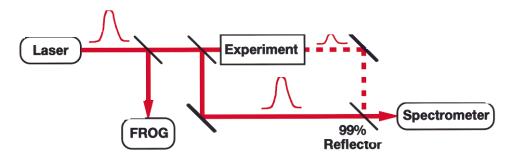


Figure 1. Apparatus for measuring ultraweak ultrashort light pulses generated in diagnostic experiments. A FROG device measures the pulse from the laser, which acts as the reference pulse for measuring the ultraweak pulse.

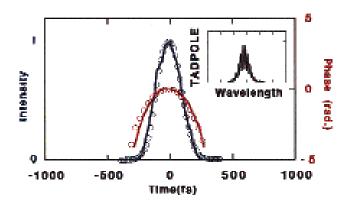


Figure 2. The measured intensity and phase versus time using TAD-POLE (circles) and, for comparison, using FROG (lines). Inset: the TADPOLE spectrum obtained by interfering the ultraweak unknown pulse with the (attenuated) reference pulse.

Combustion Technologies working group meets

Sandia hosted the most recent DOE Office of Transportation Technologies-sponsored Combustion Technologies working group meeting in April. The meetings are held semi-annually and attract experts from national laboratories, universities, and the auto companies to discuss recent research results on engine combustion issues. The meeting at Sandia included about 50 scientists and engineers.

CRF home page

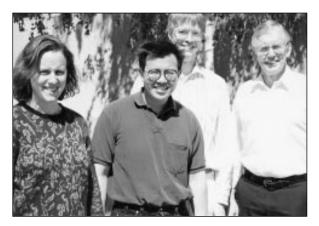
The Combustion Research Facility has a site on the Worldwide Web at http://www.ca.sandia.gov/CRF/. Certain elements are under construction and additions will be made along the way. We would appreciate your comments.

The CRF recently hosted Dr. Anatoli Jakushev, Deputy Director, and Dr. Alexandre Grebenkov, Head of Laboratory, of the Institute of Power Engineering Problems (IPEP) at the Academy of Sciences in Belarus. IPEP is collaborating with Sandia and Wheelabrator Environmental Systems, Inc. to develop biomass-fired power stations in Belarus. These facilities will be designed to utilize wood and forest litter contaminated by emissions from the Chernobyl accident and to provide low-cost electricity to Belarus. The two-year project was recently approved for funding under DOE's Industrial Partnering Program. Shown in the photo (left to right) are Larry Baxter, who leads the Sandia project; Duane Gibson, Sandia coordinator of the Belarussian activity; Steve Buckley, post doc working with Larry; Dr. Grebenkov; Don Hardesty; and Dr. Jakushev.

Vincent Perémé (left) of Nice, France, a graduate of L'Ecole Centrale in Paris, recently completed a two-month visit to the CRF working with Bob Green (right) and Pete Witze establishing an exhaust hydrocarbon measurement capability. In addition, he worked with Peter Van Blarigan studying performance of the hydrogen-fueled engine.

Sandia National Laboratories, a prime contractor to the U.S. Department of Energy, is operated by Sandia Corporation, a wholly owned subsidiary of the Lockheed Martin Corporation.

Recent Visitors



The CRF recently bid farewell to Sid Huey who spent the past two years working with Chris Shaddix, Melissa Lunden, and Don Hardesty on several fundamental investigations of the combustion of single biomass oil droplets and coal char particles. Sid accepted a staff position with Applied Materials of Santa Clara, CA. Shown (left to right) are Melissa, Sid, Chris, and Don.



Bengt Löfstedt (center), visiting from the Lund Institute of Technology (Sweden), worked on the development of infrared polarization spectroscopy. Bengt works in the combustion physics group at Lund and has been applying polarization spectroscopy to image combustion species in the visible and ultraviolet regions. While at Sandia he worked with Dave Rakestraw (left) and Jim Sherer (right) to successfully apply the technique using infrared light to probe polyatomic molecules.

Ash deposition in black liquor recovery boilers investigated

Based on previous work with both coal and biomass combustion, Scott Singuefield, a graduate student from Oregon State University (OSU), and Larry Baxter are investigating the mechanisms and rates of formation of black liquor ash deposits found in the convection passes of black liquor recovery boilers. This project is part of a collaboration with James Frederick. Professor and Chairman of Chemical Engineering at OSU, and is supported by the U.S. Department of Energy Office of Industrial Technologies. The collaboration is also supported by a consortium of industries, including every recovery boiler manufacturer in the world.

Black liquor is the by-product of the chemical pulping process used in papermaking; it is burned in boilers to recover and recycle the pulping chemicals and to generate process steam and electricity for use by the paper mill. Recovery boilers are the single most expensive items in a paper mill.

As fired, the liquor is roughly one third water, one third complex organics (lignin and other organics from the wood), and one third inorganics (mostly sodium salts). Although the primary goal is chemical recovery, combustion of black liquor is the dominant form of energy production from biomass, accounting for about 4% of the total energy production in the US.

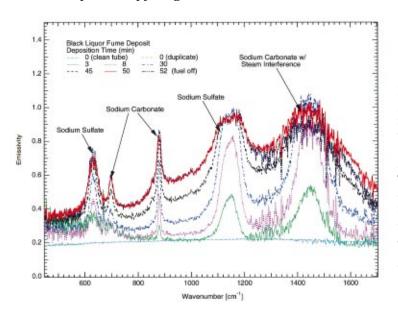
As with many condensed-phase fuels, ash management represents one of the greatest challenges in black

liquor combustion. Using Sandia's Multifuel Combustor, deposits representative of those found in commercial recovery boilers are generated on heat transfer surfaces. In situ, real-time data describing deposit mass, thickness, emissivity, composition, surface temperature, and heat flux provide the essential inputs needed to develop definitive descriptions of deposit formation. In addition, extracted gas and fume samples provide descriptions of local gas composition and small (0.01-5 μ) particle size distribution. Additional *in situ* measurements provide super-micron particle size distributions and local gas temperature.

The figure illustrates deposit composition and emissivity data during one experiment based on an FTIR-emission-spectroscopy diagnostic,

developed originally by Sandia to monitor formation of coal-ash deposits. These data indicate that sodium sulfate and sodium carbonate are the primary species in the ash deposits, with possible minor contributions from similar potassium salts. Emissivities are also seen to vary from slightly over 0.2 to about 0.9, depending on wave number, deposit thickness, and deposit temperature. Additional data suggest that these highly porous deposits, composed of relatively small particles $(< 5 \mu)$, cannot entirely be described by thermophoretic deposition rates, as has previously been supposed.

Understanding ash deposition in recovery boilers leads to ash management strategies that make optimal use of recovery boilers while minimizing emissions.



Emissivity of black liquor deposits as a function of wavenumber and deposit thickness/accumulation time. This portion of the emissivity spectrum indicates the presence of two sodium salts that dominate deposit composition, as labeled.



Published bimonthly.

For more information please contact:

William J. McLean Combustion Research Facility Sandia National Laboratories P.O. Box 969 Livermore, California 94551-0969 (510) 294-2687

ADDRESS CORRECTION REQUESTED

BULK RATE U.S. POSTAGE PAID LIVERMORE, CA 94551-0969 PERMIT NO. 234